

On Changes in the Absorption Spectra of "Didymium" Salts.

By WALTER C. BALL, M.A.

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[PLATE 1.]

There is a large amount of literature dealing with the changes produced by various agents in the absorption spectra of the rare-earth metals, amongst the most important contributions being those of de Boisbaudran,* Becquerel,† Crookes,‡ Muthmann and Stützel,§ Liveing,|| and recent papers by H. C. Jones, with various collaborators.¶

Liveing examined the effects of changes of temperature, and of concentration, on the chlorides and nitrates of erbium and "didymium."** He investigated the spectra of solutions in alcohol and in glycerol; of an ammoniacal solution of didymium tartrate (rather similar to that of an alkaline solution of didymium containing sucrose, of which the photograph is given below—photograph 10A), of acidified solutions, and also of borax glass containing didymium. He made an extensive series of photographs of these spectra, and many of the shifts of lines and bands discussed in this paper are to be seen in them, but he states that the plates had to be moved between the exposures "so that no reliance can be placed on the appearance of a shift in such photographs when the amount of such displacement is small."

In the present series of photographs, some of which are shown in the illustration appended, I have endeavoured to make the shifts of lines and bands more obvious and more easily measurable by photographing the modified spectrum in juxtaposition to that of a standard solution of didymium nitrate, and superposing the helium lines on both.

Muthmann and Stützel examined the spectrum of the acetate, and also that of the hydrogen carbonate, and concluded that Bunsen's suggestion, that the character of the absorption spectrum depends upon the molecular weight of the didymium compound, is incorrect. (This is rendered even more obvious

* 'Comptes Rendus,' vol. 88, p. 1167.

† 'Comptes Rendus,' vol. 104, pp. 777 and 1691.

‡ 'Journ. Chem. Soc. Trans.,' 1889, p. 255.

§ 'Berichte,' 1899, vol. 32, p. 2653.

|| 'Camb. Phil. Soc. Trans.,' 1900, vol. 18, p. 298.

¶ 'Amer. Chem. Journ.,' 1907, *et seq.*

** For convenience, throughout the following paper, the latter is referred to simply as didymium, although it can be resolved into neodymium and praseodymium.

by a comparison of the spectra of the acetate and trichloracetate with that of the nitrate (see Plate 1, photographs 1 and 9).)

H. C. Jones, with various collaborators, has examined the absorption spectra given by solutions in various pure solvents, and also in mixed solvents.

Liveing concludes "that the absence of any diminution of intensity of either the erbium or didymium bands by addition of acid, taken with the fact that rise of temperature does not increase their intensity, go a long way to negative the supposition that these bands are produced by metallic ions." He remarks, however, that the substantial identity of the spectra of very dilute solutions of the chloride, nitrate, and sulphate points apparently in the other direction. Of the other workers on the subject, some have reached the conclusion that ionisation will explain the facts, whereas others hold that combination of the salt, or of its ions, with the solvent is the principal factor to be considered.

For the experiments described below, I used didymium salts obtained from two sources. One sample of the nitrate contained much lead nitrate, which was almost completely removed by one extraction with absolute alcohol, which dissolved the didymium, but not the lead salt. The measurements of the lines and bands gave results agreeing very closely with those obtained by Crookes, Liveing, and other workers on the subject.

In the course of some experiments on the action of reducing agents on didymium salts, made in the hope of obtaining compounds of the metal (or rather of the neodymium and praseodymium of which the didymium consists) in a lower state of oxidation, I observed that a very marked change in the spectrum occurred on the addition of sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$ (the so-called hydrosulphite). As seen with a pocket spectroscope, this alteration consisted chiefly in a great increase in breadth and intensity of the absorption band near D, the broadening being almost wholly towards the red. In addition, others of the bands could be seen to have shifted slightly towards the red. So noticeable is the effect on the band near D, that a didymium solution diluted until its absorption spectrum is no longer visible regains this band on the addition of a little of the hyposulphite. So far as could be ascertained by eye observations, the intensity of this band is approximately trebled by this treatment. Many other reducing agents were used in place of the hyposulphite, such as zinc, magnesium, and other metals with various acids, hydroxylamine salts, titanous chloride, sulphites, etc., but in no case was any similar effect observed. As didymium salts can be fractionated into neodymium and praseodymium salts, specimens of the nitrates of these metals were obtained, and the action of hyposulphite on them examined also.

In spite of the fact that other reducing agents did not produce these changes, it seemed possible, hyposulphites being very powerful reducing

substances, that the changes might be due to a reduction of the didymium (or possibly of the contained neodymium only, for no shift of a praseodymium line could be detected with certainty in the not very satisfactory photographs obtained), but on further examination there was no evidence that this was the case. On the other hand, it was found that similar changes in the absorption spectra could be effected by adding the sodium or potassium salts of weak acids, such as acetic or nitrous. As sodium hyposulphite is the salt of a weak acid, it seemed probable that its action was an example of a general action of such salts, rather than a case of reduction by one particular reducing agent.

In order to investigate the matter more fully, a series of photographs of the absorption spectra of didymium under various conditions was made, the strengths of the acid combined with the metal, the solvent, and the concentration all being varied (Plate 1, photographs 1 to 10).

Experiments made it evident that, in order to render the photographs of such a series comparable among themselves, it would be necessary to maintain definite conditions of concentration of the didymium,* thickness of absorbing layer,† etc., for increase in the amount of didymium, due either to increase in concentration or in thickness of absorbing layer, causes a broadening of the bands, generally greater towards the red than towards the violet end of the spectrum. This effect is, however, not very marked unless the differences between two solutions are large; for example, photographs given by equal thicknesses of solutions of didymium nitrate, one containing 3 per cent. and the other 4 per cent. of Di, would appear very similar. Again, although the spectra given by a 10-cm. layer of didymium nitrate solution containing 1 per cent Di is almost identical with that given by a 1-cm. layer of a solution containing 10 per cent. Di, the only readily observable differences being that the absorption bands are wider and more hazy at their edges in the case of the stronger solution, yet, when the differences of concentration are very great, the positions of some of the lines are no longer the same in the two solutions (photographs 7 and 8 show this

* All concentrations mentioned refer to grams per 100 c.c., thus the 4-per-cent. solution contained 4 grm. of Di per 100 c.c.

† In many cases, when two spectra were to be photographed together for comparison, it was useless to give equal exposures, particularly when very different thicknesses were to be examined. In such cases the exposures were judged approximately from the relative illuminations on the camera screen, and if the resulting photographs were of very different densities, the experiment was repeated with suitably arranged exposures, as this appeared to be the only satisfactory means of obtaining comparable results. The plates were all developed for equal times, six minutes, and the other conditions were likewise uniform (*cf.* Liveing, 'Camb. Phil. Soc. Trans.,' 1900, vol. 18, p. 298 *et seq.*).

effect for concentration ratios 1:300 and 1:400, the amounts of Di in each layer being the same).

For the above reasons, the conditions in taking the appended series of photographs have been kept constant as far as possible, and are given in full.

Methods Used in Photographing the Spectra.

The source of light was a Nernst filament, the light from which was concentrated on the slit by means of an achromatic condenser. A transmission grating of 14,400 lines to the inch was used. The camera lens consisted of an achromatic telephoto combination of about 100 cm. focal length. When two photographs were to be compared, the tanks containing the absorbing solutions were placed successively in front of the slit, one half or the other of the slit being obscured by moving a screen, in which holes of the requisite size had been cut. The helium lines were then superposed on the entire photograph by the replacement of the Nernst filament by a helium tube. In this way the helium lines occupied the same position on each photograph, so that the positions and possible shifts of any absorption bands could be accurately measured. This arrangement was found to answer better than the employment of two similar sources of light, one beam passing directly to the slit, and the other after reflection by a right-angled prism attached to the slit, as, with this latter arrangement, it was not easy to obtain equality of illumination in the two photographs, which were therefore less comparable with one another.

In order to render the shifts of the lines more obvious, and as an additional check in the subsequent measurements made on the plates, most of the photographs were taken against similar standard solutions of didymium nitrate. The various absorbing solutions were contained in parallel-sided glass cells, made so as to contain various accurately measured thicknesses of liquid. In most cases these cells were fixed together with sealing-wax, and then rendered watertight with paraffin-wax.

Two pairs of photographs were generally obtained on the same plate by cutting off the light when one pair had been taken, and then raising or lowering the plate. Any slight shaking of the camera during this operation was unimportant, as the helium lines were subsequently superposed on the second pair of photographs. Panchromatic plates were used in all cases.

Eye observations were made with a telescope having a micrometer eyepiece with two moving cross-wires, and reading to 0.2 of an Ångström unit. These observations were often more useful than photographs, especially when gradual changes, produced by the addition of successive small quantities of some substance, had to be made.

Measurement of the Absorption Bands and Lines.

Nine of the absorption bands and lines in the didymium spectrum were measured, beginning with the large band near the D lines, and ending with that in the violet, near the helium line of wave-length 3889 Å.U. The other bands, especially the groups in the red, were generally too faint or too diffuse to measure accurately. These groups in the red were often absent in the photographs, and were always difficult to see, even when considerable thicknesses of concentrated solutions were used. The bands and lines measured are shown and numbered in photograph No. 1, and they fall conveniently into three groups, 1, 2, and 3, lying between the yellow helium line, D₃, wave-length 5875·6, and the green helium line 5015·7; 4, 5, and 6 between the green helium line and the blue 4471·5; and 7, 8, and 9 between this line and the violet helium line 3889. The distances between these four helium lines were measured for each plate and the number of Ångström units per centimetre thus determined for the three sections into which the spectrum was divided. The position of any particular line or band was then calculated using the value found from the helium lines between which it lay.

The positions of the centres of the maxima of absorption have been measured, and these are not in general the same as the half-way distance between the two edges. The edges of a line or band are often more or less hazy, and cannot be measured so accurately as the maximum of absorption. Line 8, especially in very dilute solution, is extraordinarily sharp and narrow, its width in a solution containing 0·0625 per cent. Di (as nitrate) was found to be four Ångströms, and it was, in reality, probably less; in consequence, it can be measured with more accuracy than the others. The mean value for its centre from eight measurements was, for solutions containing 4 per cent. Di (as nitrate), λ 4274·3 Å.U., and from four other photographs, taken last, and with some further precautions suggested during the course of experiments, the mean was 4274·0. Most of the other values given are means, and these should be correct to + or – an Ångström unit.

Tables I, II, and III (see pp. 128, 132, etc.) give the positions and shifts of the lines for several varieties of the didymium spectrum. All shifts towards the red are denoted by +, and those towards the violet –; similarly, the edge of a line or band which is nearer towards the red is described as the + edge, that nearer the violet the – edge.

Causes of the Alterations in the Spectra.

If the changes in the didymium spectrum produced by the addition of sodium or potassium acetate (see photographs 1, 2, 3, and 4) are due to a

diminution in the ionisation of the didymium salt, it would be expected that the addition of sodium or potassium salts of other weak acids would produce similar effects, for they should also reduce the ionisation. Photographs of the spectrum of didymium nitrate, before and after the addition of sodium nitrite, azide and similar salts showed that this was the case, the solid salts being added to the didymium nitrate solution (4 per cent. Di) so that the concentration of the didymium should be altered as little as possible. These effects are produced by salts of weak inorganic acids as well as by those of weak organic acids.

Again, the use of other solvents than water should entail similar effects, for the ionisation produced is generally less than that in aqueous solutions of the same strength. Photographs 5 and 6 give the spectra of solutions of anhydrous didymium nitrate (4 per cent. Di) in very carefully dried ethyl alcohol and acetone. These and other photographs of solutions in glycerol and in pyridine show that the spectra in these different solvents are very similar to one another, and that they all differ in certain respects from that given by aqueous solutions. The most important of these changes are—

(a) A shift of the bands and lines towards the red, the — edges being moved less than the + edges. Line 5 is the only exception, it exhibits a — displacement.

(b) A fusion of lines 5 and 6 (apparently due to their shifts in opposite directions, which brings them nearer together) into a broad band with two rather indistinct maxima.

(c) The two* maxima in band 2, wave-lengths 5225 and 5203 (these are their positions in the standard didymium nitrate solution, 4 per cent. Di), are replaced by a single band, centre about 5231.

Table II (p. 132) shows that these changes are approximately equal for the solvents used, and also that the spectra thus modified are very similar to those given by crystalline didymium nitrate and by the fused salt (that is, by the ordinary salt $\text{Di}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ fused in its own water of crystallisation). Further, it should be possible to produce similar changes by altering the concentration of an aqueous solution of a didymium salt: for a highly concentrated solution should be less ionised than a more dilute one, and so its spectrum should alter in the same direction as those given by solutions in alcohol, acetone, etc., and by the solid nitrate. It was not found easy to show this satisfactorily until very different concentrations were used, for the differences

* In some plates this band showed another faint maximum at 5253, and also traces of a division of the maximum with centre at 5225 into two parts with centres at 5231 and 5216.

between photographs of the spectra given by 1 cm. thickness of a nitrate solution containing 10 per cent. Di and 20 cm. of one containing 0.5 per cent Di were very slight. When, however, the concentration ratio was altered to 1:400, 0.1-cm. and 40-cm. layers of solutions containing 25 per cent. and 0.0625 per cent. Di respectively being employed, the effect was well shown (see photographs 7 and 8). The narrowness and sharpness of definition of the bands and lines in the case of the very dilute solution, and the increase in breadth and decrease in intensity and definition and also the slight + shift in the case of the very concentrated solution, can be easily seen with lines 2 and 8, photograph 8. Line 5 appears much more intense in dilute than in concentrated solution; and in very concentrated solution is practically absent (see photographs 7 and 8).* There is a curious point with regard to band 2; in the dilute solution the two maxima in this band at 5215 and 5201 are of about equal intensity and differ little in breadth (13 and 11 Å.U. respectively), but in the concentrated solution the maximum at 5215 has increased greatly in breadth towards the red, its centre now being at 5224, whereas the other maximum at 5201 has become very faint, but has not altered perceptibly in position. An exactly similar effect is produced by the gradual addition of sodium (or potassium) acetate, and can be followed by eye observation, when it is seen that the maximum in band 2 (λ 5215 in the dilute solution) nearest the red gradually moves towards the red, at the same time increasing in width, whilst the other maximum retains its position but becomes fainter until it entirely disappears, the original double band becoming single (see photographs 3 and 4).

Finally, if these effects are due to ionisation, on comparing the spectra of solutions of didymium salts, each containing the same amount of didymium, but combined with acids of different degrees of strength, similar changes should occur; the salt of the strongest acid giving a spectrum most like that given by the nitrate of didymium, whereas the salt with the weakest acid should yield a spectrum similar to that produced by the addition of sodium acetate, nitrite, etc., by the use of other solvents than water, or by the solid salt. This is shown in photograph 9, which is that of didymium trichloracetate, dichloracetate, monochloracetate, and acetate, each containing 4 per cent. Di. The trichloracetate, being the salt of an acid of the same order of strength as nitric acid, gives a spectrum exactly similar to that given by the nitrate (see Table I for measurements). The dichloracetate spectrum is very similar, but there is a slight + shift of some of the lines, seen best with

* In the three photographs which were taken of an almost saturated solution of the nitrate in water (42.3 per cent. of Di), line 5 appeared to be replaced by a wide, faint band, having three almost indistinguishable maxima of absorption.

line 8. The monochloracetate, which is the salt of a weak acid, shows greater changes in the same direction, band 2 being now single, and in the case of the acetate, the salt of a very weak acid, the alterations are very obvious. Even in the case of the acetate, however, the change to the altered spectrum does not appear to be complete, as the lines are less shifted and signs of fusion of lines 5 and 6 are only faintly seen. This was to be expected, for measurements of the conductivity of the acetate show that part of the didymium must be present in an ionised condition, the change to the non-ionised condition being therefore incomplete. The analogous spectra given by the propionate, butyrate, and lactate were also examined, but only that of the propionate, the salt of an acid still weaker than acetic, was photographed. The formate appeared to be little soluble in water.

The electrical resistances of these solutions were next determined to discover whether they altered *pari passu* with the changes in the spectrum, and, as can be seen from the appended figures, this is approximately the case.

Table I.

Solutions containing 4 per cent Di.	Relative resistance in ohms.	Position of line 8.	Shift of line 8 from 4274·0.	
Acetate	118·4	4282	+ 8	From these figures it can be seen that the resistance and the shift of line 8 alter nearly in the same ratio.
Monochloracetate	62·3	4277·6	+ 3·6	
Dichloracetate	29·2	4275	+ 1	
Trichloracetate	17·9	4273·5	—	
Propionate	167·5	4283	+ 9	
Nitrate	22·9	4274·0	—	

The figures for the resistances are only comparative, and are those given by the various solutions actually used in the spectroscopic work, when placed in a small, specially constructed electrolytic cell, with fixed electrodes.

The altered spectrum produced by the addition of sodium acetate to a solution of didymium nitrate, which appears to be essentially the spectrum of a compound, and not the spectrum of ionic didymium, reverts at once to the ordinary condition on the addition of a strong acid; these changes can be repeated at pleasure by further alternate additions of the acetate and strong acid. Addition of potassium or sodium nitrate to didymium nitrate solution also alters the spectrum in the same manner, but the effect is very much more feeble than with the acetate. The addition of strong nitric acid brings about similar changes.

Finally, a non-electrolyte, such as cane-sugar, may be added to an aqueous solution of didymium nitrate until the liquid becomes a thick syrup, and yet

the spectrum remains unaltered; a very small addition of the acetate will now produce the altered spectrum. Incidentally, this shows that viscosity and refractive index have little to do with the alterations described. There would, therefore, appear to be two distinct classes of didymium spectra.

(a) *The ionic spectrum*, that is the spectrum of the didymium ion, given by the didymium salts of strong acids, such as nitric, hydrochloric, trichloroacetic, and sulphuric, especially in very dilute solution. This spectrum is shown in photographs 7 and 8. The spectrum given by a 4-per-cent. Di solution of these salts differs but little from that given by a very dilute solution, the stronger solution giving rather broader lines and bands, with less well defined edges, and very small + shifts.

(b) *The non-ionised spectrum*, which, being in every case the spectrum of a compound, shows slight variations from compound to compound, but has a definite character. Such spectra are those produced by adding the sodium or potassium salt of a weak acid to the didymium salt of a strong acid (photographs 1, 2, 3, and 4), those given by the didymium salt of a weak acid (photographs 9, C and D), those given by solutions of didymium salts in certain solvents, such as ethyl alcohol, etc. (photographs 5 and 6), and those given by the nitrate, either crystalline or melted (photograph 11).

These spectra are characterised by the great increase in breadth and in intensity of band 1; disappearance of the maximum 5203 in band 2 (it appears, however, in the crystal spectrum); similar changes in band 3; the fusion of lines 5 and 6, and a general shift of bands and lines towards the red (line 5, which has an opposite shift, excepted). The fusion of lines 5 and 6 does not appear to be so constant as the other effects, and is absent in the spectrum produced by the addition of sodium hyposulphite (photographs 1 and 2), which is probably essentially that of non-ionised didymium hyposulphite.*

Although these "non-ionised" spectra are similar to one another in general character, they show many minor differences, especially in the positions of the maxima in band 1 (these cannot easily be seen in the photographs, but have been examined by eye), and in the positions of the edges of this band. Although alkalis at once precipitate the hydroxide from solutions of didymium salts, yet, by the addition of sucrose, it is possible to prevent this precipitation and to obtain the spectrum of didymium in alkaline solution (see

* Some attempts were made to obtain the spectrum of a didymium salt in a non-ionising solvent, but without much success, as the salts used proved to be nearly insoluble in such solvents. However, the trichloroacetate was slightly soluble in chloroform, and in 20 cm. thickness of this solution bands 1 and 2 could be observed. They were rather diffuse, and consequently difficult to measure, but showed + shifts of about 15.

photograph 10). This spectrum presents quite exceptional characters, some of the lines being enormously shifted. Possibly in this case the didymium is contained in the negative ion. The same remarks apply to the very similar photographs given by didymium glass.

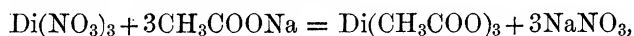
Liveing states that the anhydrous chloride, DiCl_3 , is insoluble in absolute alcohol, but samples of the nitrate which I heated to 170° — 180° C., until there was no further change in weight (they lost very slightly more than the theoretical amount of water for the formula $\text{Di}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), dissolved almost completely in very dry alcohol, dried over lime for some weeks, and then over metallic calcium; they were also soluble in pure acetone.* These solutions gave spectra similar to those produced by dissolving the hydrated salt in alcohol and in acetone respectively. These spectra again differ so little from that of the crystalline nitrate, that it seems possible that the absorbing constituent in all is the same, and that they are all essentially the spectra of non-ionised $\text{Di}(\text{NO}_3)_3$. The spectra of these solutions in alcohol or acetone rapidly revert to that of an aqueous solution, on the addition of water, so that the spectrum of didymium nitrate in a mixture containing 50 per cent. ethyl alcohol and 50 per cent. water is practically that of an aqueous solution.

On comparing very concentrated solutions of didymium salts in water with very dilute ones, it appears that the chief alterations in the spectra take place on passing from a very high concentration to one rather lower, and that further dilution produces only trifling changes in the spectrum, although ionisation, judging from the conductivity changes, is by no means complete. Thus the changes in the spectrum between a solution of the nitrate containing 42 per cent. Di and one containing 4 per cent. Di are much greater than those between concentrations of 4 per cent. and 0.0625 per cent. (the chloride spectrum changes less with dilution, according to Liveing and others, and according to my own observations; I have found also that the conductivity alters more with dilution in the case of the nitrate than with the chloride). If the spectrum of the crystal is that of $\text{Di}(\text{NO}_3)_3$, modified very little by the water with which it is combined, and if that of a very dilute aqueous solution is that of the didymium ion, it may be a possible explanation of these observations that the nitrate is very

* I was able to make up a solution of the anhydrous nitrate in anhydrous ethyl alcohol containing 21 per cent. of Di. A layer of this, 0.165 cm. thick, was photographed together with a 61.3 cm. layer of a solution containing 0.057 per cent., the quantities of absorbing didymium being the same, but the concentrations in the ratio 1 : 370. There was much less difference between the two spectra than in the corresponding case for aqueous solutions, the lines being shifted little, if at all, relatively to one another in the two spectra.

considerably ionised, even in a fairly strong solution, and that the subsequent changes on further dilution, which seem to be much greater in the case of the electric conductivity than in the absorption spectrum, may be due to an increase in mobility of the didymium ion, and not in its relative numbers.

The spectra of some of these solutions are almost certainly the combined spectra of two substances. That it is so may be seen on reference to photographs 3 and 4, which show the effect of adding to a very dilute (0.07 per cent. Di) aqueous solution of didymium nitrate the exact amount of sodium acetate required by the equation



and also twice this amount. In photograph 3, with the smaller amount of acetate, line 8 is seen to be doubled, the centres of its components being 4274 and 4281. The component at 4274 is therefore identical in position with line 8 of the spectrum of aqueous didymium nitrate, whilst that at 4281 is probably due to non-ionised didymium acetate (line 8 in an aqueous solution of didymium acetate, containing 4 per cent. Di, having its centre at 4282 (see Table I)). In photograph 4, addition of another equivalent of sodium acetate has caused the latter component to increase in intensity, and that at 4274 almost to disappear, effects which would be expected if more didymium acetate has been formed by the excess of sodium acetate present; again, line 8 in a solution of didymium nitrate containing 4 per cent. Di appears composite, as though it consisted of the sharp line of the very dilute solution superposed on the wider, less intense line of the very concentrated solution. Similarly, line 8 in the spectrum of a very dilute solution of the anhydrous nitrate in carefully dried ethyl alcohol is possibly double. On the other hand, the spectrum of a dilute solution in water would seem to be that of a single substance, for the lines become increasingly narrow and definite as the dilution is increased. I expected to obtain a distinctly composite spectrum on mixing quantities of the acetate and trichloracetate containing equal amounts of didymium, but obtained a spectrum having rather hazy lines and bands and resembling that of the acetate rather than that of the trichloracetate.

Table II.

The following table gives the positions of certain of the lines, of their edges, and the extent of their shifts, for didymium nitrate in various solvents, and, for comparison, the corresponding data for the crystalline and fused salt, and for an alkaline solution. The most dilute solution in water (0.0625 per cent. Di) is taken as the standard, and the shift of any line is the number of Ångström units through which its centre is shifted from the position it occupies in this 0.0625-per-cent. solution.

C denotes the position in a line or band where the absorption is most intense E the position of the edges, and W the width of a line or band. All shifts towards the red are marked +, those towards the violet —. The edge of a band or line towards the red is called the + edge, that nearer the violet the — edge.

Solution of didymium nitrate in—	Line 8.	Shift of 8.	Lines 5 and 6.	Shift of 5.*	Shift of 6.
Water— 0.0625 p.c. Di ...	C. 4273.6 E. 4276 : 4272 W. 4.1	0	4751 : 4688	0	0
4.0 „ ...	C. 4274.0 E. 4280 : 4269 W. 11	+0.5	4757 : 4694	+6	+6
25 „ ...	C. 4276.4 E. 4285 : 4271 W. 14	+3	4753 : 4692 Lines very faint.	+2	+4
Ethyl alcohol— Containing 2 p.c. Di as anhy- drous salt	C. 4282 E. 4291 : 4275 W. 16	+9	4739 : 4704 Lines 5 and 6 have coalesced into wide band with above maxima of absorption.	—12	+16
Glycerol— Containing 4 p.c. Di as hydrated salt	C. 4284 E. 4289 : 4270 W. 19 In this case, unlike the others, the absorption is much greater near the + edge.	+10	Lines 5 and 6 have coalesced to a broad band with maxima at 4749 : 4701	—2	+13
Acetone— 4 p.c. Di as an- hydrous salt	C. 4286 E. 4289 : 4276 W. 13	+12	Lines 5 and 6 have coalesced to a broad band with maxima at 4746 : 4704	—5	+16
Pyridine	C. 4284 Additional faint, rather narrow, line appears at 4308.	+10	Lines 5 and 6 have coalesced to a broad band with maxima at 4783, 4744 : 4708	—7	+20

Solution of didymium nitrate in—	Line 8.	Shift of 8.	Lines 5 and 6.	Shift of 5.	Shift of 6.
Di(NO ₃) ₃ ·6H ₂ O fused	C. 4278 E. 4285 : 4268 W. 17	+ 4	Lines 5 and 6 have coalesced to a broad band with maxima at 4737 : 4698	— 14	+ 10
Solid salt— Di(NO ₃) ₃ ·6H ₂ O...	C. 4283	+ 9	Lines 5 and 6 have coalesced to a broad band with maxima at 4737 : 4700	— 14	+ 12
Solution of didymium nitrate— 2 p.c. Di, containing cane-sugar and NaOH	Very sharp maximum with diffuse part surrounding it. C. 4317 Additional faint line at 4330.	+ 43	Lines 5 and 6 are replaced by a broad band with maxima at 4792 : 4739	+ 41	+ 51

* The maxima in the broad band which replaces lines 5 and 6 are rather indistinct and difficult to measure. In consequence, the shifts of lines 5 and 6 are less accurately measured than those of line 8; this applies especially to the case of line 5.

Table III.—Positions of Lines and Bands in various Didymium Absorption Spectra.

C. = The centre of a line or band (or, if the band be multiple, of the maxima of absorption in the band).
 E. = The positions of the edges.
 W. = The width.

The + edge of a line or band is that edge nearer the red.
 The — " " " " " violet.
 All measurements are in Ångström units.

Region of spectrum.	Number of line or band.	Aqueous solution of didymium nitrate, 0.0625 per cent. Di, 40 cm. layer.	Aqueous solution of didymium nitrate, 25 per cent. Di, 0.1 cm. layer.	Aqueous solution of didymium nitrate, 4 per cent. Di, 3 cm. layer.	Crystal of $\text{D}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$, 0.1 cm. to 0.2 cm. thick.	Didymium glass.	Aqueous solution of didymium nitrate, 4 per cent. Di, + $\text{Na}_2\text{S}_2\text{O}_4$.	Aqueous solution of didymium nitrate, 2 per cent. Di, with sucrose and caustic soda.
Orange	1	Sharply defined, contained four maxima E. 5740—5707 Centres of maxima— 5783 5751 5735 5715 W. 83	Compared with 0.0625-per-cent. solution, is wider in each direction, edges are less sharp and maxima less intense E. 5841—5695 Centres of maxima— 5795 5762 5735 W. 146	In 3 cm. layer no maxima could be seen. They were visible in thinner layers C. 5774 E. 5855—5694 W. 161	This band appears to be divided into two portions. One, an intense part with sharp edges at 5846—5708, W. 138. The other a fainter part extending to 5987 and having two rather faint maxima with centres at about 5973 and 5944	Band very wide, and most intense portion at + side E. 5942—5684 W. 258 Maxima having centres at— 5860 5827 5741	Very wide and intense E. 5987—5697 C. 5842 W. 290	Very wide, both edges shifted towards red. E. 6028—5706. W. 322.
Green	2	Two very sharp, narrow, lines, close together C. of 1st line, 5215 E. " " 5224—5211 W. " " 13 C. of 2nd line, 5201 E. " " 5207—5196 W. " " 11	Two lines as in 0.0625-per-cent. solution, but the first of these has doubled in width, and the second has decreased in intensity C. of 1st line, 5224 E. " " 5235—5210 W. " " 25 C. of 2nd line, 5204 E. " " 5207—5197 W. " " 10	Multiple band E. 5335—5198 W. 138 Centres of maxima— 5253 5231 5216 5203 The separation between the maxima at 5231 and 5216 is very slight and they generally appear as single maximum with C. at 5224	Band with four maxima, the two middle maxima being only faintly separated. Band is intense Centres of maxima— 5250 5229 5220 5197	Single band, very faint, wide and diffuse C. 5268	Band with two maxima E. 5344—5204 W. 140 Centres of maxima— 5270 5232	Band with three ill-defined maxima having centres at— 5285. 5277. 5267.
Green	3	Double, fainter than band 2 C. of 1st line, 5117 E. " " 5138—5104 W. " " 32 C. of 2nd line, 5087 E. " " 5093—5081 W. " " 13	Very faint band with two maxima Centres of maxima— 5113 5086 E. of band, 5125—5082 Total W. of band 43	Double, fainter than band 2; diffuse edges E. 5149—5082 W. 67 Centres of maxima— 5120 5091	Band with two maxima. Weaker than band 2 Centres of maxima— 5113 5087	Single band, very faint, wide and diffuse C. 5130	Single band E. 5154—5098 C. 5127 W. 56	Very diffuse single band. C. 5142.

Blue ...	4	Fairly sharp line C. 4316	C. 4320	C. 4321 W. 19	Strong; narrow C. 4331	Possible faint trace of this band detected	C. 4330 W. 31	Wide, ill-defined. C. 4353.
Blue ...	5	C. 4751	Very faint indeed C. 4753	C. 4758 W. 21	Lines 5 and 6 are re- placed by band with two maxima having their centres at 4737 and 4700	Absent	Faint C. 4761 W. 25	Lines 5 and 6 have merged into a band having two maxima with centres at 4792 and 4739.
Blue ...	6	C. 4638	C. 4632	C. 4694 W. 14				
Blue ...	7	Wide, rather diffuse C. 4436	Wider and more diffuse than in 0.0625-per-cent. solution C. 4439	Wide, diffuse edges C. 4437 W. 38	Wide. Edges indis- tinct C. about 4440	Very faint trace, with centre about 4470	C. 4456 W. 47	Very faint trace. Centre about 4470.
Violet	8	Extremely sharp and narrow C. 4273.6 E. 4276-4272 W. 4.1	Wider and less sharp than in 0.0625-per-cent. solution C. 4276.4 E. 4285-4271 W. 14	Narrow; maximum in- tensity near-edge C. 4274.0 W. 10	Sharply defined and narrow C. 4283	Very faint, wide, diffuse. C. 4301. Is possibly the maximum in a wide, very faint band	Wide C. 4289 W. 21.	Very sharp max. C. at 4317. Much weaker one. C. at 4330. Diffused part at each side.
Violet	9	—	—	Wide, diffuse C. 4023 W. 28.	—	—	—	—

Conclusions.

(A) That the chief changes produced by dilution of an aqueous solution of didymium nitrate occur when a very concentrated solution is diluted slightly and that further dilution, although the didymium salt still alters in electric conductivity, produces comparatively small effects.

(B) That conditions which would be expected to reduce the ionisation of didymium salts, such as combination of the didymium with a weaker acid, addition of the sodium or potassium salt of a weak acid, solution in a solvent of less general ionising power than that of water, or increase of concentration of the salt in solution, all produce fairly similar changes in the absorption spectra.

There are some curious points which I hope to investigate further, particularly as to why the spectrum of the nitrate alters so slightly between concentrations of say 10 per cent. Di to 0.05 per cent. Di, whereas the conductivity alters considerably. Further investigations, with very dilute solutions, might also throw some light on the effects produced by the gradual addition of sodium acetate and other salts, particularly on the changes produced in band 1. These consist in the production of transient maxima of absorption within the band, and also of a minimum of intensity of the whole band, followed by a large increase.

I wish to express my cordial thanks to Mr. Abram, of the Physics Department, Guy's Hospital Medical School, for his very kind and valuable help, especially in the taking and measuring of the photographs, and to Dr. Veley for much valuable advice.

DESCRIPTION OF PLATE.

All spectra are reproduced half scale of originals. Some of the finer details, in particular the maxima in bands 1 and 2, and the doubling of line 8 in photographs 3, A, and 4, A, though very obvious in the originals, are much less clearly seen in the reproductions.

Photograph 1. Effect of adding excess of potassium acetate.

A. Aqueous solution of didymium nitrate, 4 per cent. Di, with excess of potassium acetate.

B. The same, without the potassium acetate.

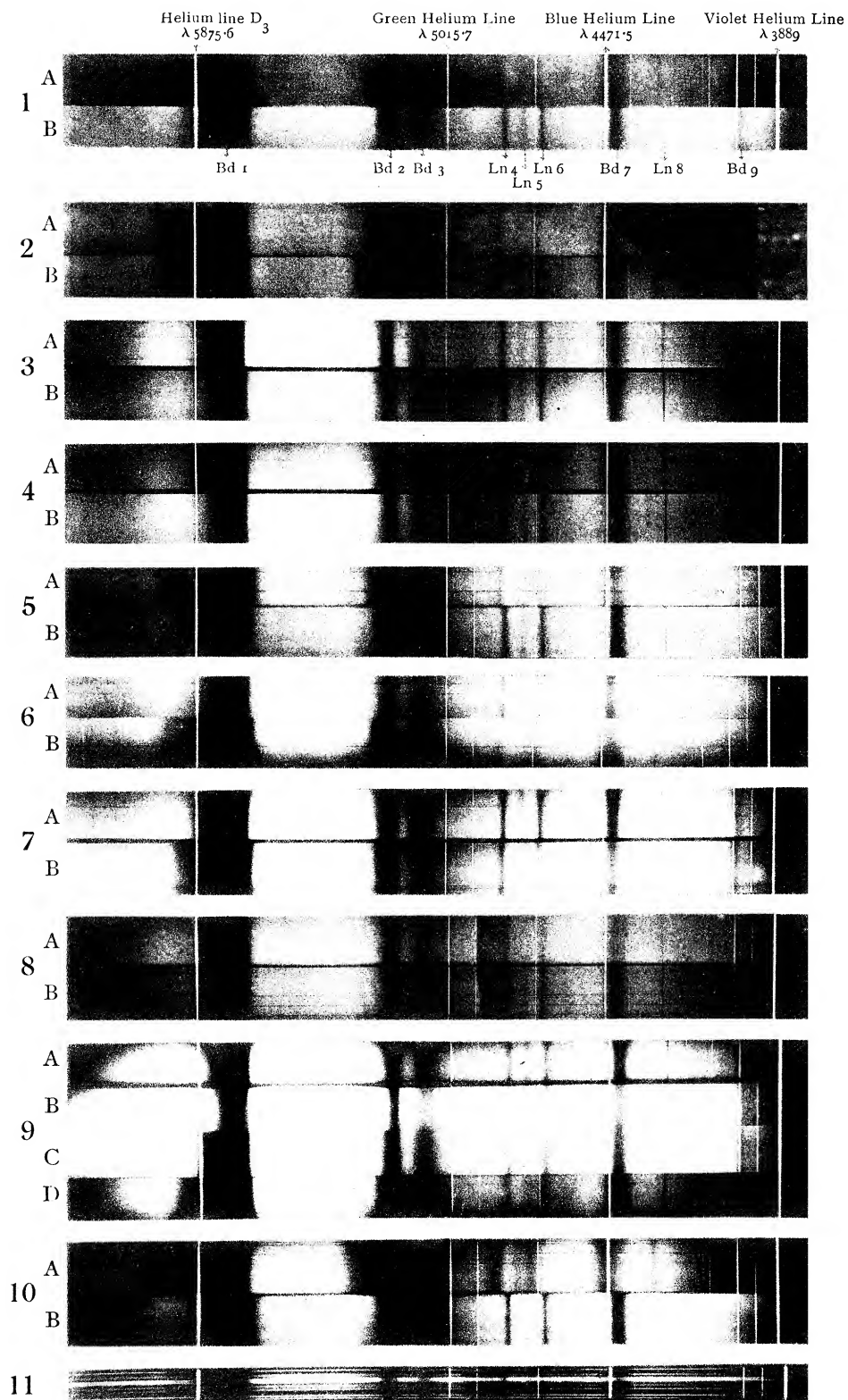
In each case, 20 secs. exposure; 3 cm. layer; width of slit, 0.01 cm. Helium exposure, 120 secs.

Photograph 2. Comparison of effect of potassium acetate with that of sodium hyposulphite.

A. Aqueous didymium nitrate, 4 per cent. Di, with excess of potassium acetate, as 1, A.

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Exposures, 30 secs. Other conditions as in 1.



Photograph 3. Effect of sodium acetate in dilute solution.

A. 61.3 cm. layer of aqueous didymium nitrate, 0.07 per cent. Di,
containing one equivalent of sodium acetate.

B. The same, but without the acetate.

Exposures, 250 secs. ; width of slit, 0.005 cm. Helium exposure, 240 secs.

Photograph 4—

A. As 3, A, but with two equivalents of acetate.

B. As 3, B.

Other conditions exactly as in 3.

Photograph 5. Solution of anhydrous didymium nitrate in ethyl alcohol.

A. Anhydrous nitrate in well-dried ethyl alcohol, 2 per cent. Di.
Exposure, 60 secs.

B. Aqueous solution of the same strength. Exposure, 50 secs.

3 cm. layers ; width of slit, 0.01 cm. Helium exposure, 180 secs.

Photograph 6—

A. Aqueous solution of didymium nitrate, 4 per cent. Di.

B. Solution of the anhydrous salt in acetone, 4 per cent. Di.

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Photograph 7. Spectra of dilute and of concentrated aqueous solutions.

A. 61.3 cm. layer of aqueous didymium nitrate, 0.1413 per cent. Di.
Exposure, 100 secs.

B. 0.205 cm. layer of aqueous didymium nitrate, 42.25 per cent. Di.
Exposure, 85 secs.

Width of slit, 0.005 cm. Helium exposure, 240 secs. These contained the same
amount of didymium in the absorbing layers, but in concentration ratio 1 : 300.

Photograph 8. As 7, but concentration ratio 1 : 400.

A. 0.1 cm. layer of aqueous didymium nitrate, 25 per cent. Di.
Exposure, 50 secs.

B. 40 cm. layer of aqueous didymium nitrate, 0.0625 per cent. Di.
Exposure, 210 secs.

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Photograph 9. Effect of variation in strength of acid combined with the didymium.

A. Aqueous didymium trichloracetate, 4 per cent. Di.

B. „ dichloracetate, „

C. „ monochloracetate, „

D. „ acetate, „

Exposures, 20 secs. ; 3 cm. layers ; width of slit, 0.01 cm. Helium exposure, 120 secs.

Photograph 10. Alkaline solution of didymium.

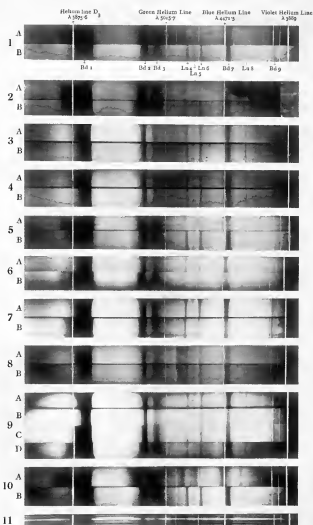
A. Aqueous solution of didymium (as nitrate) with sucrose and
caustic soda, 2 per cent. Di. Exposure, 90 secs.

B. Aqueous didymium nitrate, 2 per cent. Di. Exposure 45 secs.

3 cm. layers ; width of slit, 0.005 cm. Helium exposure, 180 secs.

Photograph 11. Crystal of $\text{Di}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Thickness, 0.1—0.2 cm.

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